

Date of Application:

August 23, 1995

Application Number:

Patent Application JP7/215074

Applicant:

Asahi Glass Company Ltd.

【Type of Document】 PETITION FOR PATENT APPLICATION

【Reference No.】 950467

【Filing Date】 August 23, 1995

【Addressee】 Commissioner, Patent Office

【International Patent Classification】 C23C 14/34

【Title of the Invention】
TARGET AND PROCESS FOR ITS PRODUCTION, AND METHOD FOR
FORMING A FILM HAVING A HIGH REFRACTIVE INDEX

【Number of Inventions Stated in Claim(s)】 7

【Inventor(s)】

 【Name】 Otojiro Kida

 【Address or Residence】 Asahi Glass Company Ltd.
Chuo Kenkyusho
1150, Hazawa-cho, Kanagawa-ku,
Yokohama-shi, Kanagawa

 【Name】 Akira Mitsui

 【Address or Residence】 Asahi Glass Company Ltd.
Chuo Kenkyusho
1150, Hazawa-cho, Kanagawa-ku,
Yokohama-shi, Kanagawa

 【Name】 Eri Suzuki

 【Address or Residence】 Asahi Glass Company Ltd.
Chuo Kenkyusho
1150, Hazawa-cho, Kanagawa-ku,
Yokohama-shi, Kanagawa

【Patent Applicant(s)】

 【Identification No.】 000000044

 【Name or Company Name】 Asahi Glass Company Ltd.

 【Representative】 Hiromichi Seya

【Representative(s)】

 【Identification No.】 100090918

 【Patent Attorney】

【Name or Company Name】	Kenji Senmyo	
【Telephone Number】	03-3218-5647	
【Identification of Fees】		
【Prepayment account No.】	009830	
【Amount of Payment】	21,000 yen	
【List of Submitted Items】		
【Name of item】	Specification	1
【Name of item】	Abstract	1
【General Authorization No.】	9004246	
【Burden of Proof】	Yes	

- 1 -

【TYPE OF DOCUMENT】 SPECIFICATION

【TITLE OF THE INVENTION】

TARGET AND PROCESS FOR ITS PRODUCTION, AND METHOD FOR
FORMING A FILM HAVING A HIGH REFRACTIVE INDEX

【SCOPE OF THE CLAIM(S)】

【Claim 1】

A process for producing a sputtering target, which comprises roughening the surface of a substrate, forming an undercoat made of a metal or alloy on the substrate by plasma spraying, and then forming a ceramic layer as a target material on the undercoat wherein a ceramic powder which is made in a semi-molten state in a high temperature plasma gas in a reducing atmosphere, is transported and deposited onto the undercoat by the plasma gas, wherein, as the undercoat, a layer having a thermal expansion coefficient intermediate between the thermal expansion coefficient of the ceramic layer and the thermal expansion coefficient of the substrate, and/or a layer having a thermal expansion coefficient close to the thermal expansion coefficient of the ceramic layer, is formed, and as the ceramic layer, a layer comprising Nb_2O_x ($4 < x < 5$) as the main component is formed.

【Claim 2】

The process for producing a sputtering target according to Claim 1, wherein a cylindrical substrate is used as the substrate.

【Claim 3】

The process for producing a sputtering target according to Claim 1 or 2, wherein the ceramic layer has a resistivity of at most 10 Ωcm at room temperature.

【Claim 4】

A sputtering target comprising a substrate having the surface roughened, an undercoat made of a metal or alloy formed on the substrate, and a ceramic layer as a target material formed on the undercoat, wherein, as the undercoat, a layer having a thermal expansion coefficient intermediate between the thermal expansion coefficient of the ceramic layer and the thermal expansion coefficient of the substrate, and/or a layer having a thermal expansion coefficient close to the thermal expansion coefficient of the ceramic layer, is used, and as the ceramic layer, a layer comprising Nb_2O_x ($4 < x < 5$) as the main component is used.

【Claim 5】

The sputtering target according to Claim 4, wherein a cylindrical substrate is used as the substrate.

【Claim 6】

The sputtering target according to Claim 4 or 5, wherein the ceramic layer has a resistivity of at most 10 Ωcm at room temperature.

【Claim 7】

A method for forming a film having a high refractive index by sputtering, wherein, as a sputtering target, the sputtering target as defined in Claim 4, 5 or 6 is used.

[DETAILED DESCRIPTION OF THE INVENTION]

[Technical Field to which the Invention Belongs]

The present invention relates to a target to be used for forming a transparent thin oxide film having a high refractive index by direct current (DC) sputtering, and a process for its production, and a method for forming a film having a high refractive index by using such a target.

[Prior Art]

Optical applications of thin oxide films start from single layer type heat reflecting glasses and antireflection films and extend to various fields including, for example, multi-layer type antireflection coatings, reflection enhancing coatings, interference filters and polarizing films, which are designed to permit lights having certain specific wavelengths to reflect or pass selectively therethrough. Further, a study has been made to insert a transparent electroconductive film or a film of e.g. metal or electroconductive ceramics having various functions such as electroconductivity and heat reflection properties as a part of a multi-layer film to obtain a multi-layer film having a function such as an antistatic, heat reflecting or electromagnetic wave shielding function provided.

The spectral characteristics of a multi-layer film are optically designed by using refractive indexes n and thicknesses of the respective layers, as parameters, and it is common to employ a combination of a high refractive index film and a low refractive index film. To realize excellent optical properties, the larger the difference in the

refractive index between the high refractive index film and the low refractive index film, the better. As such a high refractive index film, titanium dioxide ($n=2.4$) cerium dioxide ($n=2.3$), zirconium dioxide ($n=2.2$), niobium pentoxide ($n=2.1$), tantalum pentoxide ($n=2.1$) or tungsten trioxide ($n=2.0$) is, for example, known. Further, as a low refractive index film, silicon dioxide ($n=1.46$) or magnesium fluoride ($n=1.38$) is, for example, known.

Such films can be formed, for example, by a vacuum vapor deposition method or a coating method. However, by such a film-forming method, it is difficult to form a uniform film over a substrate having a large area, and when a substrate having a large area, such as a glass for buildings or automobiles, CRT, or a flat display, is required, sputtering is used in many cases. Among various sputtering methods, DC sputtering utilizing direct current discharge is most suitable for forming a film over a large area.

When a high refractive index film is to be formed by DC sputtering, it is common at present to employ so-called reactive sputtering wherein a metallic target having electroconductivity is subjected to sputtering in an atmosphere containing oxygen. However, there has been a problem that the film-forming speed of a thin film obtainable by this method is very slow, whereby the productivity is poor, and the cost tends to be high.

JP-A-62-161945 proposes a process for producing a non-electroconductive ceramic sputtering target made of various oxides by water plasma spraying. This target is a target for

radio frequency (RF) sputtering, and the target itself is an insulating material. An electroconductive target material can not be obtained by this method. Further, this target has had drawbacks that, unless some measures such as an undercoating is taken, it is likely to undergo cracking or peeling as the temperature rises during sputtering, whereby film formation under a stabilized condition tends to be difficult. Further, there has been a drawback such that the film forming speed is very slow.

To satisfy these requirements, the present inventors have proposed a sputtering target for a high refractive index thin film of a ceramic sintered body in Japanese Patent Application JP7-087160. However, recently, a sputtering target is required to have a complex shape, and a highly efficient planar target having the target thickness partially changed, is required. By a method for obtaining a sintered body by a common sintering method, it is difficult to produce a target having a complex structure or various shapes, and such a target is prepared by a long process including steps of mixing starting materials, sintering, processing and bonding, whereby substantial jigs are required for its production.

Further, in sputtering over a glass sheet with a large area for buildings, the film-forming speed is increased by applying a high power for sputtering to increase the productivity, whereby cooling of the target tends to limit the film-forming speed, and troubles such as cracking of the target, peeling, etc, are likely to occur.

A new magnetron type rotary cathode is known wherein such drawbacks have been overcome (JP-A-58-500174). This is of a type wherein a magnetic field generating means is provided inside of a cylindrical target, and sputtering is carried out while rotating the target and cooling the target from inside. By the use of such a cylindrical target, a large power per unit area can be applied as compared with a planer type target, whereby film formation at a high speed is said to be possible.

Preparation of a target material on a cylindrical target holder has heretofore been commonly carried out when the target material is a metal or alloy. In the case of a metal target, multi-layer film coatings of e.g. its oxide, nitride, carbide, etc. are formed in various sputtering atmospheres. However, it has had drawbacks that the coating films are likely to be damaged by different types of atmospheres, whereby films having desired compositions can hardly be obtainable, and, in a case of a low melting metal target, the target is likely to undergo melting when the power applied is excessive. Under these circumstances, a ceramic target material has been desired.

JP-A-60-181270 proposes a process for producing a ceramic sputtering target by spraying. However, the process has had problems that the sprayed coating can not be made sufficiently thick, as the difference in thermal expansion between the ceramics and the substrate metal is large, and the adhesion tends to deteriorate by thermal shock during its use, thus leading to peeling.

Further, a method has been proposed in which a ceramic sintered body is formed into a cylindrical shape and bonded to a substrate by means of indium metal. However, this method is difficult and costly.

[Problems that the Invention is to Solve]

It is an object of the present invention to provide an electroconductive sputtering target which can be formed into any desired shape and which is capable of forming a high refractive index film at a high speed by DC sputtering, a process for its production, and a method for forming a high refractive index film using such a target.

It is another object of the present invention to provide a high density target for a rotary cathode sputtering which is high in the degree of freedom from the viewpoints of production and use and by which a high refractive index film can be formed at a high speed, and a method for its production, and a method for forming a high refractive index film using the target.

[Means of Solving the Problems]

The present invention provides a process for producing a sputtering target, which comprises roughening the surface of a substrate, forming an undercoat made of a metal or alloy on the substrate by plasma spraying, and then forming a ceramic layer as a target material on the undercoat wherein a ceramic powder which is made in a semi-molten state in a high temperature plasma gas in a reducing atmosphere, is transported and deposited onto the undercoat by the plasma gas, wherein, as the undercoat, a layer having a thermal

expansion coefficient intermediate between the thermal expansion coefficient of the ceramic layer and the thermal expansion coefficient of the substrate, and/or a layer having a thermal expansion coefficient close to the thermal expansion coefficient of the ceramic layer, is formed, and as the ceramic layer, a layer comprising Nb_2O_x ($4 < x < 5$) as the main component is formed.

The present invention also provides a sputtering target comprising a substrate having the surface roughened, an undercoat made of a metal or alloy formed on the substrate, and a ceramic layer as a target material formed on the undercoat, wherein, as the undercoat, a layer having a thermal expansion coefficient intermediate between the thermal expansion coefficient of the ceramic layer and the thermal expansion coefficient of the substrate, and/or a layer having a thermal expansion coefficient close to the thermal expansion coefficient of the ceramic layer, is used, and as the ceramic layer, a layer comprising Nb_2O_x ($4 < x < 5$) as the main component is used.

The present invention further provides a method for forming a high refractive index film using the above target.

In the present invention, for the formation of the ceramic layer, the ceramic powder used for spraying is made in a semi-molten state by means of a plasma spraying apparatus and deposited on a substrate, so that a target layer for a sputtering target is directly formed.

Accordingly, the process does not require a molding step, a sintering step, a processing step to form a complex

structure or shape, or a bonding step. In the present invention, description is given mainly to the step for obtaining a ceramic powder used for spraying. In a case of a complicated compound which is not readily available in the form of a ceramic powder, such a compound may be chemically synthesized or may be prepared by using a solid phase reaction. The ceramic powder used for spraying (hereinafter referred to simply as the ceramic powder) may be pulverized or granulated, and further classified, so that it is adjusted to have a readily flowable particle size suitable for spraying.

The resistivity of the ceramic layer at room temperature is preferably at most $10 \Omega\text{cm}$ to conduct discharge stably during the sputtering. If the resistivity exceeds $10 \Omega\text{cm}$, the discharge is not stable, such being undesirable.

If the ceramic layer of the present invention is represented by Nb_2O_x , the range of x is $4 < x < 5$. If x is 5, the ceramic layer is in a completely oxidized state and thereby electrically insulating, whereby DC (direct current) sputtering can not be conducted. Further, if x is not higher than 4, the ceramic layer is chemically unstable and not preferable.

In the ceramic powder, other components may be contained in such an amount that the objects and effects of the present invention are not spoiled. However, it is preferred to limit such components as small as possible.

The ceramic powder to be used in the present invention can be prepared by the following method. Namely, a Nb_2O_5

powder having an average particle size of at most 10 μm is weighed in a predetermined amount and mixed in a wet system for at least 1 hour in a ball mill using a binder such as PVA and water as a dispersing medium, to obtain a slurry, which is then dried by a spray drier to obtain a powder having a particle size of from 20 to 100 μm . The composition of this powder is Nb_2O_5 , but becomes Nb_2O_x ($4 < x < 5$) during the subsequent plasma spraying in a reducing atmosphere.

In another method, ethanol is used as the above mentioned dispersing medium, and a Nb_2O_5 powder is mixed with ethanol in a wet system for at least one hour by means of a ball mill in the same manner as described above, and the mixture is dried by an evaporator and then calcined in an inert atmosphere at a temperature of from 1,000 to 1,200°C, followed by classification to obtain a powder having a particle size of from 20 to 100 μm . The composition of this powder is Nb_2O_x ($4 < x < 5$) by calcination, but is further reduced during the subsequent plasma spraying in a reducing atmosphere.

If the particle size exceeds 100 μm , such a ceramic powder tends to be hardly made in a semi-molten state in a high temperature plasma gas, and if it is smaller than 20 μm , such a powder is likely to be dispersed in the high temperature plasma gas and thus tends to be hardly deposited on the substrate.

For the substrate, various metals or alloys, such as stainless steel, copper or titanium, may be used. Prior to the plasma spraying of a ceramic powder for the target material, it is essential to roughen the surface of the

substrate, for example, by sand blasting by means of abrasive grains made of Al_2O_3 or SiC in order to improve the adhesion. Otherwise, it is also preferred to process such a substrate surface to form a V-groove, followed by sand blasting by means of abrasive grains made of Al_2O_3 or SiC , in order to improve the adhesion.

After roughening the substrate surface, an undercoat made of a metal or alloy may be formed in order to reduce the difference in the thermal expansion between the target material to be sprayed and the substrate and to improve the adhesion so as to be durable against peeling by mechanical and thermal impacts.

As such an undercoat, a layer (hereinafter referred to as layer A) having a thermal expansion coefficient intermediate between the substrate and the target material, and/or a layer (hereinafter referred to as layer B) having a thermal expansion coefficient close to the target material, may be used. It is particularly effective to form both layers to have a structure of the substrate/layer A/layer B/ceramic layer. It is preferred to form the undercoat also by plasma spraying.

Even when the undercoat is made solely by layer A or layer B, the adhesive force of the ceramic layer to the substrate can be improved, since the metal or alloy is not brittle and has high elasticity. The thermal expansion coefficient of layer B is most suitably within a range of $\pm 2 \times 10^{-6}/^\circ\text{C}$ of the thermal expansion coefficient of the ceramic layer.

As the material for the undercoat, an electroconductive powder of e.g. Mo, Ti, Ni, Nb, Ta, W, Ni-Al, Ni-Cr, Ni-Cr-Al, Ni-Cr-Al-Y or Ni-Co-Cr-Al-Y may be employed. The thickness of the undercoat is preferably from 30 to 100 μm .

It is necessary to change the material for the undercoat depending upon the thermal expansion coefficient of the ceramic layer. The thermal expansion coefficient of e.g. copper or stainless steel which is useful as a substrate, is from 17×10^{-6} to $18 \times 10^{-6}/^{\circ}\text{C}$, and the thermal expansion coefficient of titanium is $8.8 \times 10^{-6}/^{\circ}\text{C}$.

For example, for the ceramic layer (the thermal expansion coefficient: 6×10^{-6} to $9 \times 10^{-6}/^{\circ}\text{C}$) in the present invention, the preferred thermal expansion coefficient of the undercoat layer A is from 12×10^{-6} to $15 \times 10^{-6}/^{\circ}\text{C}$, and as such a material, Ni, Ni-Al, Ni-Cr, Ni-Cr-Al, Ni-Cr-Al-Y or Ni-Co-Cr-Al-Y, may, for example, be mentioned.

Further, the preferred thermal expansion coefficient of the undercoat layer B is from 4×10^{-6} to $11 \times 10^{-6}/^{\circ}\text{C}$, and as such a material, Mo, Nb, Ta, W or Ti, may, for example, be mentioned.

Further, the adhesion can be further improved by providing an undercoat layer having the composition gradually changed from a material having a thermal expansion coefficient close to the target material to a material having a thermal expansion coefficient close to the substrate, selected among such undercoat materials. Further, when the substrate is made of titanium, the undercoat may be made

solely of layer B, since the thermal expansion coefficient is close thereto.

On such an undercoat, a ceramic powder which is made in a semi-molten state in a high temperature plasma gas, preferably a high temperature plasma gas such as Ar or Ar+H₂, in a reducing atmosphere, is transported and deposited onto the undercoat by such a gas, to form a ceramic layer which serves as a target material. In this manner, a ceramic layer comprising Nb₂O_x as the main component, is obtained.

By the formation of the ceramic layer, it is possible to form a uniform and dense ceramic layer which undergoes less fluctuation of the chemical composition or mineral composition of the ceramic powder.

By forming the undercoat, the difference in thermal expansion between the ceramic layer and the substrate can be reduced, whereby a ceramic layer which is free from peeling even with a thickness as thick as from 2 to 10 mm, can be formed.

Also at the time of forming the undercoat, it is preferred to form it by plasma spraying in a high temperature plasma gas, preferably in a high temperature plasma gas in a reducing atmosphere, for the same reason as described above.

Further, as the plasma spraying method, water plasma spraying is more effective. This water plasma spraying is a method wherein a high pressure water stream supplied to a torch firstly forms a cylindrical eddy current at the cylindrical section, and in this state, a voltage is applied between a carbon cathode and an iron rotary anode to let

direct current arcs form to evaporate and decompose water at the inner surface of the eddy current to form a plasma state thereby to generate plasma arcs continuously, and such plasma arcs are constricted by the revolving cylindrical water current to increase the energy density and eject a stabilized high temperature high speed plasma jet flame from a nozzle by rapid thermal expansion of the plasma. This spraying method is applicable likewise.

A uniform transparent film can be formed at a high speed, when sputtering is carried out by using the target of the present invention in an Ar atmosphere or in a mixed atmosphere of Ar and O₂ under a pressure of from 1×10^{-3} to 1×10^{-2} Torr. In this case, the target of the present invention brings about no hysteresis phenomenon which is a non-continuous change in the film forming speed or the discharge current or voltage due to change of the oxygen partial pressure when a metal target is employed. Accordingly, control of the film forming speed during the film formation will be very easy in the present invention.

The target of the present invention has electroconductivity and thus is useful for DC sputtering, whereby a uniform, transparent high refractive index film can be formed at a high speed over a large area. The target of the present invention is useful also for RF sputtering.

[Operation]

When a metal target is used for forming a metal oxide film, the film forming speed or the sputtering voltage changes abruptly and non-continuously in a hysteresis fashion

due to a change of the oxygen gas partial pressure before or after the change from an absorbing film to a transparent film having the stoichiometrical composition, or before or after the change from a transparent film to an absorbing film. Accordingly, to obtain a transparent film constantly, it is necessary to introduce oxygen gas substantially excessively relative to the metal atoms.

Whereas, the target of the present invention is composed of an oxide, and is slightly deficient in oxygen as compared with the stoichiometric composition. Accordingly, film formation of a transparent metal oxide film can be carried out simply by supplementing the oxygen slightly deficient as compared with the stoichiometric composition. Besides, when the target of the present invention is employed, no change like the above mentioned hysteresis phenomenon will take place, whereby the amount of the oxygen gas to be supplied can be minimized to the required minimum or reduced to a level close to the required minimum. Thus, deposition of excess oxygen atoms on the target surface, which is believed to cause deterioration of the film forming speed, can be reduced, and the film forming speed can be increased.

When a target is produced by a spraying method as in the present invention, the oxide powder is made in a molten state and then quenched and solidified so that the sprayed material will be laminated on the substrate. At that time, crystal alignment will form in the sprayed material, since there is a difference in the crystal growth rate of crystal faces. Namely, the face at which the surface density is low and the

growth rate is high, crystallizes quickly in the direction along the substrate, and crystal alignment will necessarily form, so that the face at which the surface density is high and the growth rate is low, becomes the sputtering surface.

On the other hand, it is believed that the higher the surface density, the better the sputtering efficiency, and the higher the sputtering speed. Accordingly, this crystal alignment is believed to be one of the factors for the high film forming speed by the present invention.

Further, with a sputtering target thus prepared, thermal conductivity from the ceramic layer to the substrate and further to the cathode electrode, is good, and the ceramic layer is firmly bonded to the substrate. Accordingly, even when a high sputtering power is applied to increase the film forming speed, cooling can sufficiently be carried out, and peeling or cracking of the ceramic layer due to abrupt heat shock will not take place, and a large electric power per unit area can be applied.

Further, even when an erosion zone of the ceramic layer became thin, such a zone can readily be regenerated to the initial state by plasma spraying a ceramic layer of the same material to such a portion which became thin. Further, it is easy to provide a distribution in thickness of the ceramic layer depending upon any desired position, and it is thereby possible to control the thickness distribution of a thin film to be formed by providing a temperature distribution or a distribution in strength of the magnetic field at the target surface.

Further, when a cylindrical substrate is employed, the entire surface will be the erosion zone of the target, whereby there is a merit that the utilization efficiency of the target is high as compared with the planer type.

【Examples】

Example 1

High purity Nb_2O_5 powder (average particle size: at most $10\text{ }\mu\text{m}$) was mixed in a wet system for 1 hour in a ball mill using PVA binder and water as a medium, and the obtained slurry was granulated by means of a spray drier to obtain a ceramic powder having a particle size of from 20 to $100\text{ }\mu\text{m}$.

Using a copper planer substrate (thermal expansion coefficient: $17 \times 10^{-6}/^\circ\text{C}$) having a diameter of 6 inches as a target metal holder, the outer surface was roughened by sand blasting by means of Al_2O_3 abrasive grains to obtain a roughened surface.

Then, an alloy powder of Ni-Al (weight ratio of 8:2) was plasma-sprayed (using a metoko sprayer) under a reducing atmosphere to form an undercoat layer A (thermal expansion coefficient: $12.5 \times 10^{-6}/^\circ\text{C}$) having a thickness of $50\text{ }\mu\text{m}$. This plasma spraying under a reducing atmosphere was carried out using $\text{Al}+\text{H}_2$ gas as the plasma gas at a flow rate of 42.5 l/min by applying a power of 35 kV at 700 A to instantaneously heat the alloy powder of Ni-Al by the $\text{Ar}+\text{H}_2$ gas plasma of from $10,000$ to $20,000^\circ\text{C}$ and to transport the alloy powder together with the gas onto the target metal holder to let it solidify thereon. The coating film was formed by repeating an

operation of moving the plasma spraying gun right and left and up and down.

Then, using a Ni metal powder, plasma spraying was carried out in the same manner as above to form an undercoat layer B (thermal expansion coefficient: $7.1 \times 10^{-6}/^{\circ}\text{C}$) having a thickness of 50 μm . Further, using the above mentioned ceramic powder, plasma spraying was carried out under the same reducing atmosphere to form a ceramic layer having a final thickness of 5 mm.

The ceramic layer of the obtained target was cut out from the metal substrate, and the density and the resistivity were measured. Further, the obtained ceramic layer was pulverized in an agate mortar and heated to $1,100^{\circ}\text{C}$ in air, whereby the weight increase was measured. Assuming that after the heating in air, the powder became completely oxidized TiO_2 , the oxygen content of the ceramic layer was calculated from the weight increase. The results are shown in Table 1.

EXAMPLE 2

Mixing by means of a ball mill was conducted in the same manner as in Example 1 except that ethanol was used as the medium instead of the PVA binder and water. Then, drying was conducted by means of an evaporator, and a bulky powder obtained by calcining in an Ar atmosphere at from $1,000$ to $1,200^{\circ}\text{C}$, was classified to obtain a ceramic powder having a diameter of from 20 to 100 μm . Then, in the same manner as in Example 1, a target was obtained and the density, resistivity and oxygen content in the ceramic layer of the target were measured. The results are shown in Table 1.

EXAMPLE 3 TO 6

The target of Example 2 was mounted on a magnetron DC sputtering apparatus, and film formation of a Nb_2O_5 film was carried out. The film formation was carried out under such conditions that the applied power was DC 1kW, the back pressure was 1×10^{-5} Torr, and the sputtering pressure was 2×10^{-3} Torr. As the sputtering gas, a gas having argon and oxygen mixed in various oxygen concentration, was used. The proportion of the oxygen gas in the sputtering gas was from 10 to 40 volume%. If the oxygen is lower than 10 volume%, the film will be an absorptive film, and in order to obtain a transparent film, oxygen was required to be at least 10 volume%.

As the substrate on which a Nb_2O_5 film is to be formed, a soda lime glass was used. No intentional heating was applied to the substrate. The sputtering was carried out so that the film thickness would be about 100 nm. During the sputtering, the electrical discharge was very stable, and film formation was carried out under a stable condition even by DC sputtering. After the film formation, the film thickness was measured by means of a feeler type film thickness measuring apparatus. Further, the refractive index of the film was measured by an ellipsometer. The wavelength of light employed at that time, was 633 nm. The proportion of the oxygen gas in the sputtering gas, the film forming speed (unit: nm/minute) and the refractive index of the film are shown in Table 2. All of the films obtained were transparent and showed no light absorption.

EXAMPLES 7 TO 8 (COMPARATIVE EXAMPLES)

As Example 7, using a metal titanium target instead of the target of Example 3, film formation by sputtering was carried out in the same manner. The proportion of oxygen gas in the sputtering gas was 20 volume%. In the case of a titanium target, if oxygen is lower than 20 volume%, the film becomes an absorptive film, and in order to obtain a transparent film, oxygen was required to be at least 20 volume%. Accordingly, sputtering was carried out at an oxygen concentration of 20 volume % which was the oxygen proportion at which a transparent film could be obtained and the film forming speed was highest.

Further, as Example 8, using a metal niobium target instead of the target of Example 3, film formation by sputtering was carried out in the same manner. In the case of metal niobium target, the sputtering was carried out at an oxygen concentration of 30 volume % for the same reason as mentioned above.

As is evident from Table 2, a transparent Nb_2O_5 film having a high refractive index can be formed at a high speed by using the target of the present invention.

EXAMPLE 9

In Example 1, a copper cylindrical target holder having an inner diameter of 50.5 mm, and outer diameter of 67.5 mm and a length of 406 mm, was attached to a lathe, and its outer surface side was threaded and further surface roughened by sand blasting by means of Al_2O_3 abrasive grains to form a roughened surface, and otherwise, in the same manner as in

Example 1, a target was prepared. And, in the same manner as in Example 1, the density, the resistivity and the oxygen content of the ceramic layer of the target were measured. The results were the same as in Example 1.

EXAMPLE 10

A target was prepared in the same manner as in Example 9 except that ethanol was used as the medium instead of the PVA binder and water used in Example 9 and the ceramic powder was obtained by the method of Example 2, and the density, resistivity and oxygen content of the ceramic layer of the target were likewise measured. The results were the same as in Example 2.

EXAMPLES 11 TO 14

Film formation of a Nb_2O_5 film was carried out in the same manner as in Example 3 to 6 except that the target in Example 10 was used as the target.

During the sputtering, the discharge was very stable, and film formation was carried out under a stabilized condition even by DC sputtering. Further, all of the obtained films were transparent and showed no light absorption.

The refractive index of the film as in Examples 3 to 6. Table 2 shows the proportion of the oxygen gas in the sputtering gas, the film-forming speed (unit: nm/minutes) and the refractive index of the film. As evident from Table 2, transparent Nb_2O_5 films having a high refractive index can be formed at a high speed by using the target of the present invention.

【Table 1】

	Density (g/cc)	Resistivity (Ω cm)	x in Nb ₂ O _x
Example 1	4.30	0.15	4.98
Example 2	4.40	0.12	4.93

【Table 2】

	Target	Proportion of oxygen gas	Film- forming speed	Refractive index
Example 3	Nb ₂ O _x planer type	10 vol%	97	2.3
Example 4	Nb ₂ O _x planer type	20 vol%	80	2.3
Example 5	Nb ₂ O _x planer type	30 vol%	48	2.3
Example 6	Nb ₂ O _x planer type	40 vol%	35	2.3
Example 7	Ti	20 vol%	6	2.4
Example 8	Nb	30 vol%	13	2.3
Example 11	Nb ₂ O _x rotary cathode type	10 vol%	105	2.3
Example 12	Nb ₂ O _x rotary cathode type	20 vol%	90	2.3
Example 13	Nb ₂ O _x rotary cathode type	30 vol%	54	2.3
Example 14	Nb ₂ O _x rotary cathode type	40 vol%	42	2.3

【Effects of the Invention】

By using the sputtering target of the present invention,
a transparent film having a high refractive index can be

formed at a high speed by DC sputtering. Further, with the target of the present invention, the oxygen partial pressure of the sputtering atmosphere can be reduced, thus providing a merit that abnormal discharge such as arcing can be reduced. Accordingly, by using the target of the present invention, a film having a high refractive index can be produced at a high speed and under a stabilized condition.

The target prepared by the process of the present invention is uniform, highly dense and strong against thermal shock. According to the process of the present invention, a target having an optional shape can easily be produced without requiring conventional shaping, sintering, processing or bonding step.

Further, with the sputtering target of the present invention, the target can be regenerated by plasma spraying a spraying powder of fresh target material having the same composition to a consumed portion after use, such being economically advantageous.

By using the sputtering target of the present invention, the cooling effect during the sputtering is high, whereby even if the sputtering power is increased, cracking or breakage of the target will not take place, and film forming at a high speed can be carried out under a stabilized condition at a low temperature. Thus, the productivity of not only display elements or CRT but also large surface glasses for buildings or automobiles, can remarkably be improved.

【 TYPE OF DOCUMENT】 ABSTRACT

【 SUMMARY】

【 PROBLEMS TO BE SOLVED】

It is intended to provide an electroconductive sputtering target which can be formed into any desired shape and which is capable of forming a high refractive index film at a high speed by DC sputtering, a process for its production, and a method for forming a high refractive index film using such a target.

【 MEANS OF SOLVING THE PROBLEMS】

A method for producing a sputtering target which comprises roughening the surface of a substrate and forming an undercoat having a specific thermal expansion coefficient and a ceramic layer containing Nb_2O_x ($4 < x < 5$) as a main component in this order on the substrate by plasma spraying.

【 SELECTED FIGURE】 No Selected Figure